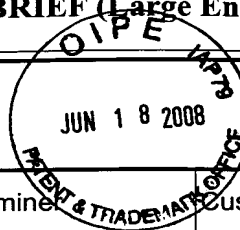


## TRANSMITTAL OF APPEAL BRIEF (Large Entity)

Docket No.  
5017

In Re Application Of: Song, et al.



Application No.	Filing Date	Examiner	Customer No.	Group Art Unit	Confirmation No.
10/747,668	December 29, 2003	Ahmed, Hasan Syed	48226	1615	1567

Invention: Natural Pearlescent Odor Reduction

COMMISSIONER FOR PATENTS:

Transmitted herewith is the Appeal Brief in this application, with respect to the Notice of Appeal filed on:  
**April 9, 2008**

The fee for filing this Appeal Brief is: \$510.00

- ☐ A check in the amount of the fee is enclosed.
- ☐ The Director has already been authorized to charge fees in this application to a Deposit Account.
- ☒ The Director is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 05-1070. I have enclosed a duplicate copy of this sheet.
- ☐ Payment by credit card. Form PTO-2038 is attached.

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

  
Signature

Dated: June 17, 2008

Stuart D. Frenkel  
Reg. No. 29,500  
Frenkel & Associates, P.C.  
3975 University Drive, Suite 330  
Fairfax, VA 22030  
Phone: 703-246-9641  
Facsimile: 703-246-9646

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on

June 17, 2008

(Date)

  
Signature of Person Mailing Correspondence

Stuart D. Frenkel

Typed or Printed Name of Person Mailing Correspondence

CC:



## TRANSMITTAL OF APPEAL BRIEF (Large Entity)

Docket No.  
5017

In Re Application Of: Song, et al.

Application No.	Filing Date	Examiner	Customer No.	Group Art Unit	Confirmation No.
10/747,668	December 29, 2003	Ahmed, Hasan Syed	48226	1615	1567

Invention: Natural Pearlescent Odor Reduction

COMMISSIONER FOR PATENTS:

Transmitted herewith is the Appeal Brief in this application, with respect to the Notice of Appeal filed on:  
**April 9, 2008**

The fee for filing this Appeal Brief is: \$510.00

- ☐ A check in the amount of the fee is enclosed.
- ☐ The Director has already been authorized to charge fees in this application to a Deposit Account.
- ☒ The Director is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 05-1070. I have enclosed a duplicate copy of this sheet.
- ☐ Payment by credit card. Form PTO-2038 is attached.

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

  
Signature

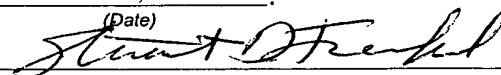
Dated: June 17, 2008

Stuart D. Frenkel  
Reg. No. 29,500  
Frenkel & Associates, P.C.  
3975 University Drive, Suite 330  
Fairfax, VA 22030  
Phone: 703-246-9641  
Facsimile: 703-246-9646

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on

June 17, 2008

(Date)



Signature of Person Mailing Correspondence

Stuart D. Frenkel

Typed or Printed Name of Person Mailing Correspondence

CC:



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Song, et al.	Art Unit: 1615
Serial No: 10/747,668	Examiner: Ahmed, Hasan Syed
Filing Date: December 29, 2003	
Title: <i>Natural Pearlescent Odor Reduction</i>	Atty. Docket No.: 5017

**APPEAL BRIEF**

Commissioner of Patents  
and Trademarks  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This is an appeal from the Final Rejection of claims 1-20, dated  
January 11, 2008.

**REAL PARTY IN INTEREST**

The real party in interest of this application is BASF Catalyst, L.L.C.

**RELATED APPEALS AND INTERFERENCES**

U.S. Serial No. 10/908,503, filed May 14, 2005 is related to the  
technology of the present application and has been assigned Appeal No.  
2008-2392.

06/18/2008 WABDELRI 00000054 051070 10747668  
01 FC:1402 510.00 DA

06/18/2008 WABDELRI 00000014 051070 ~~10747668~~

01 ~~FC:1401~~ -510.00 DA

### STATUS OF THE CLAIMS

Claims 1-20 have been Finally rejected and are being appealed.

### STATUS OF AMENDMENTS

No amendment under Rule 116 has been filed.

### SUMMARY OF CLAIMED SUBJECT MATTER

The claimed invention is directed to deodorizing a natural pigment obtained from fish scales. As stated in the application at page 5, lines 2-9, the initial steps of the process of separating natural pearlescent pigment from fish and forming the pearlescent paste are known in the art and do not form part of the novelty of the invention. As disclosed at page 5, lines 10-15, the first step of the process involves separating the native guanine crystals from the fish scales, water washing and then extracting the crystals. In the Background of the Invention at page 1, line 18 through page 2, line 1, it is initially stated that it is known to recover pearlescent crystals from fish scales. As stated at page 2, lines 17-23, it has been found that the natural crystallized guanine from the fish scales can contain impurities which result in an unpleasant odor in the products formulated therewith. The unpleasant odor often persists even after several bleaching and washing steps.

In the presently claimed invention and as set forth in independent claim 1, the deodorization of the pigment derived from fish scales is achieved by contacting the pigment with a complex metal hydride. This is described initially at page 8, lines 1-3. Claim 2 recites that the pigment comprises guanine which is disclosed at previously mentioned page 5, lines 10-19. The formation of an aqueous pigment paste, claim 3, is described at page 5, line 17 through page 8, line 3. The complex metal hydride preferably used to treat the pigment derived from fish scales is sodium borohydride as set forth in claims 4 and 6 and as described at page 8, lines 3-5. The sodium borohydride is preferably added to the pigment paste as a solid powder and in amounts ranging from 0.5 to 10 wt.%, and preferably in an amount of 1 wt.% relative to the pigment paste, as set forth in claims 9, 10, and 11. Support for each of

these limitations is set forth at page 8, lines 12-18. To help with the treating procedure and to cause foaming and off gassing of the mixture of the complex metal hydride and the pigment paste, a weak acid, claim 5, such as an organic acid, claim 7, and, in particular, acetic acid, claim 8 is added to the mixture. This is specifically described at page 9, lines 5-24 of the specification, as well as page 10, lines 15-21. The weak acid is added in amounts of 0.5 to 10 wt.% of the pigment paste, and preferably in an amount of 1 wt.% of the pigment paste as set forth in claims 12 and 13 and disclosed at page 9, lines 5-9 of the specification. It is also important that the weak acid be added to the mixture of pigment paste and sodium borohydride no more than 3 hours after the mixture is formed, claim 14 and as disclosed at page 9, lines 17-21. The deodorized pigment paste is useful in cosmetic formulations as set forth in claims 18-20, and as set forth at page 12, lines 11-19.

#### GROUND OF REJECTION TO BE REVIEWED ON APPEAL

Claims 1, 2 and 4 have been Finally rejected under 35 U.S.C. 102(b) as being anticipated by JP 51149211A ("Saiga"). Saiga is applied as disclosing a method of improving odor from natural sources comprising the use of a borohydride. The Examiner states that the Saiga reference discloses amines as the source of the odor. The Examiner states that although Saiga does not disclose the fish scales of claim 1 or the guanine of claim 2, the Examiner concludes that amines are inherently the source of odor in guanines and fish scales.

Claims 1-8, 10 and 14-17 have been Finally rejected under 35 U.S.C. 103(a) as being unpatentable over Saiga in view of JP2003088337A ("Hiroshi"). Saiga is applied as teaching a method of improving odor from natural sources. Saiga is admitted as different from the instant application in that it does not teach the weak acid of claims 5, 7, 8, and 14-17. The Examiner states, however, that the use of weak organic acids to reduce the odor of fish scale products was known in the art before the instant application was filed, as taught by Hiroshi (paragraph 0011). The Examiner admits that although Hiroshi does not teach the acetic acid of claims 8 and 17, citric acid

and phosphoric acid as set forth in paragraph 0011 of Hiroshi are deemed to be functional equivalents of acetic acid.

The primary reference to Saiga is also admitted as differing from the instant application in that it does not teach the fish scale derived paste of instant claims 3, 14 and 15. Hiroshi is applied as forming a fish scale derived paste by mixing acidic water with ground fish scales, paragraphs 0015 and 0016. Hiroshi is further applied as teaching that adding weak organic acids to fish scale derived products sharply reduces the smell of fish scales, paragraph 0048. The Examiner concludes that it would have been obvious to one of ordinary skill in the art at the time the invention was made to disclose a method of reducing the odor of fish scale derived products using complex metal hydride and weak acid as taught by Saiga in view of Hiroshi.

Claims 1, 9 and 11-13 have been Finally rejected under 35 USC 103 as being unpatentable over JP 51149211A (Saiga) in view of JP 2003088337A (Hiroshi). The Examiner states that Saiga teaches a method of improving odor from natural sources and Hiroshi teaches a method of reducing the odor of fish scale derived products using weak organic acids. The Examiner admits that the prior art does not explicitly teach all the instant claimed percentages, but concludes it would have been obvious to one of ordinary skill in the art at the time the invention was made to determine suitable percentages through routine or manipulative experimentation to obtain the best possible results, as these are variable parameters attainable within the art. The Examiner also states that, generally, differences in concentration will not support the patentability of subject matter encompassed by the prior art unless there is evidence indicating such concentration is critical. The Examiner states that the Applicants have not demonstrated any unexpected or unusual results which accrue from the instant percentage ranges.

Claims 1 and 18-20 have been Finally rejected under 35 USC 103(a) as being unpatentable over Saiga in view of Hiroshi and further in view of U.S. Patent No. 4,486,334 (Horiuchi). The Examiner states that Saiga teaches a

method of improving odor from natural sources and Hiroshi teaches a method of reducing the odor of fish scale derived products using weak organic acids. The Examiner states that Saiga and Hiroshi differ from the claimed invention in that the references do not teach a cosmetic formulation. The Examiner states, however, that fish scale derived cosmetic formulations were known in the art before the instant application was filed as explained by Horiuchi, column 1, lines 11-31. The Examiner concludes it would have been obvious to one of ordinary skill in the art at the time the invention was made to disclose a cosmetic formulation derived from fish scales as taught by Horiuchi.

### ARGUMENT

Claims 1, 2, and 4 have been rejected under 35 U.S.C. 102(b) as being anticipated by JP 51149211A ("Saiga").

To reject a claim on the basis of anticipation over a reference, the reference must teach each and every limitation of the claimed invention. The claimed invention as recited in claim 1 is directed to contacting a pigment, which has been derived from fish scales with a complex metal hydride. Saiga does not teach a process of treating a pigment derived from fish scales with a complex metal hydride. Saiga is directed to treating a long-chain aliphatic amine derived from a natural fat or oil with a complex metal hydride such as the claimed sodium borohydride. Since the applied reference does not teach the claimed limitation of deodorizing a "pigment derived from fish scales", the applied reference cannot be used to properly reject claims 1, 2, and 4 by anticipation under 35 U.S.C. 102(b).

The Examiner argues that the Saiga reference reads on instant claims 1, 2, and 4 as they are currently drafted, and states that the recitation of "fish scales" has not been given patentable weight because the recitation occurs in the preamble. The Examiner states that a preamble is generally not accorded any patentable weight where it merely recites the purpose of a process or the intended use of a structure, and where the body of the claims does not depend on the preamble for completeness but, instead, the process steps or structural limitations are able to stand alone. Appellants have no argument

with the Examiner's discussion of when a preamble is not accorded any patentable weight. However, the instances in which the Examiner states that the preamble is not given any patentable weight are not present in the appealed claims. In appealed claim 1, a "pigment derived from fish scales" is the object that is being treated. The claim does not set forth an intended use, does not set forth a purpose of a process, and the body of the claim certainly depends upon the preamble for completeness inasmuch as the process is directed to treating "said pigment", which has antecedent basis in the preamble which recites "deodorization of pigment derived from fish scales" with a complex metal hydride. The Examiner simply cannot ignore the preamble in this instance when the process claims herein are directed specifically to acting on the subject of the preamble, i.e. pigment derived from fish scales. The claimed invention is not directed to contacting any object with a complex metal hydride. The treatment of long chain aliphatic amines derived from a natural fat or oil, as discussed in the applied reference, does not anticipate the claimed process.

The Examiner also argues that the present invention is directed to removing unpleasant odor in the fish scales and that the amines are the source of the unpleasant odor. In fact, the present application at page 2, lines 17-20 states that the naturalized crystalline guanine, which is obtained from the fish scales, may contain impurities, believed to be amines which can cause deterioration of, and as well, provide an unpleasant odor in the products formulated therewith. The Examiner states that the applied reference to Saiga "also targets amines in order to neutralize odor produced by natural fat and oils using the same compound as that of claims 1 and 4". The Examiner has incorrectly interpreted the applied reference. In the applied reference to Saiga, the aliphatic amines are not the source of an unpleasant odor but are the material to be purified. Thus, in the present claims, a pigment derived from fish scales is being purified whereas in the applied reference, long chain aliphatic amines derived from a natural fat or oil are being purified. As stated at page 3, last paragraph of the translation of Saiga, it is stated that "Oxidizable impurities, such as aldehydes and ketones, are contained in aliphatic amines using natural fats and oils as raw materials. They are odor



sources or coloring precursors”. As stated at page 4, lines 4-5 of the translation, “the oxidizable impurities contained in the aliphatic amines must be removed”. At page 7, last paragraph of the translation of Saiga, it is stated “large amounts of oxidizable impurities, such as aldehydes and ketones, are contained in the aliphatic amines using natural fats and oils”. The reference goes on to state that esters are produced by a reaction between the impurities and the borohydride alkali metal salt. Accordingly, the applied reference is not targeting amines, but is purifying amines. The pigment derived from fish scale is not a long-chain aliphatic amine but is guanine, claim 2, which is a nucleotide, not an aliphatic amine. Moreover, although not claimed, the present invention seeks to neutralize the amines which are impurities in the pigment. In Saiga, the long-chain amines are purified by removing carbonyl compounds by reaction with the complex metal hydride. The Examiner concludes that Saiga uses the same compound (borohydride) as the claimed invention to react with the same target (amine). This statement is not correct as the target of the claimed invention are amine impurities, whereas the target in the applied reference are carbonyl impurities. As such, the applied reference to Saiga does not anticipate instant claims 1, 2, and 4.

Claims 1-8, 10, and 14-17 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Saiga in view of JP 2003/088337A (“Hiroshi”).

First, the primary reference is not at all concerned with deodorizing a pigment derived from fish scales, as discussed above. Again, the primary reference to Saiga is concerned with chemically reducing carbonyl compounds that are odor sources in long chain aliphatic amines and their derivatives obtained from natural fats and oils with borohydride compounds. The patent does not remotely suggest treating a pigment, a solid, derived from fish scales with the complex metal hydride to reduce the odor of amine impurities.

The secondary reference does not make up for the deficiencies of the primary reference. The secondary reference is an attempt to form a liquid derived from fish scales and to deodorize the liquid. At page 4 of a translation

of Hiroshi, it states “fish scales dissolve in acidic water and also that this fish scale solution has a considerably reducible fish odor”. The process of Hiroshi is unlike the process of Saiga which purifies long-chain amines. Accordingly, the applied references are not properly combinable.

Moreover, the process of Hiroshi is unlike the process of the present invention which treats the pearlescent crystals taken from the fish scales, and is not directed to forming a fish scale liquid. In the presently claimed invention, a weak acid is added to the mixture of pigment and complex metal hydride to cause foaming and off-gassing from the mixture. As stated at page 9 of the application, the addition of a weak acid neutralizes the finished product and the liquid waste water providing improved odor reduction. Further, it has been found that the off-gassing which is achieved during the addition of the weak acid, appears to be needed to provide successful odor reduction. The combination of references does not suggest the benefit of adding both complex metal hydride and a weak acid to a paste of fish scale-derived pigment.

The Examiner submits that Applicants provide no evidence in the disclosure that off-gassing results in odor reduction.

Quite the contrary to the Examiner’s statement, the application clearly sets forth the advantages for adding the weak acid, in particular, acetic acid to produce foaming and off-gassing. As stated at page 9, lines 16-19 of the application, “delaying the acid neutralization prevents or reduces the significant off-gassing, which appears to be needed to provide successful odor reduction”. The next statement states that “if the mixture is allowed to sit too long, the addition of the acid does not result in the desired off-gassing or foaming action which is needed”. At page 10, lines 8-14 of the application, a theory is suggested “that the odor contamination in the pearlescent pigment material derived from fish is influenced by amine compounds, and that the borohydride-acid system which is used to treat the pearlescent pigment paste is thought to affect the odor diminution through a first reduction of odoriferous compounds including lower amines, such as dimethylamine and a second

weak Lewis acid-based reaction to release the reduced compounds". Thus, the specification clearly points to the need for both a sodium borohydride addition and acetic acid addition. Inasmuch as the primary reference to Saiga is not at all directed to treating the same material as that claimed, and since Hiroshi is not concerned with treating the same material as Saiga, and does not remotely suggest the enhanced odor reduction using both borohydride and acetic acid, the combination of Saiga with Hiroshi cannot be said to render the claimed process obvious and unpatentable.

The Examiner admits that the secondary reference does not even teach acetic acid. More importantly, the secondary reference teaches an addition of acid to the aqueous mixture of fish scales to dissolve the fish scales. The patent does not otherwise suggest extracting any crystalline pigment from the dissolved fish scales. The Examiner states that although Hiroshi does not teach the acetic acid of instant claims 8 and 17, the citric acid and phosphoric acid disclosed by Hiroshi are deemed to be functional equivalents of acetic acid. On the contrary, phosphoric acid is a very strong mineral acid and is used in Hiroshi to dissolve the fish scales. In the present invention, a weak acid is used to add to the mixture of crystals derived from fish scales, water and borohydride to cause off-gassing and improve odor reduction. The use of an acid to dissolve fish scales in the secondary reference is not all applicable to the presently claimed process.

The combination of references is improper as the applied references are directed to non-analogous art. The primary reference is directed to purifying long-chain aliphatic amines and the secondary reference to forming a fish scale liquid. Moreover, the combination of references does not remotely suggest the treatment of a pigment derived from fish scales with a complex metal hydride and weak acid as claimed. The primary reference is concerned with purifying amines derived from natural fats and oils, and the secondary reference is concerned with dissolving fish scales to form a fish scale solution in water and does not remotely suggest using the crystalline material from the fish scales as a pigment or the deodorization of such crystalline material. The secondary reference while concerned with deodorizing the dissolved liquid

derived from fish scales does not suggest use of a borohydride but instead, utilizes a cyclodextrin to aid in the deodorization process. In view of the fact that both the primary and secondary references are directed to deodorizing a liquid and not to deodorizing a pigment derived from fish scales, the combination of references cannot remotely suggest or render obvious the claimed invention.

Claims 1, 9, and 11-13 are rejected under 35 U.S.C. 103(a) as being unpatentable over Saiga in view of Hiroshi.

As stated above, the combination of the primary and secondary references do not remotely suggest the claimed process. The primary reference is concerned with chemically purifying long-chain aliphatic amines obtained from natural fats and oils not treating pigment derived from fish scales. The secondary reference is not concerned with treating a pigment derived from fish scales but is concerned with dissolving the fish scales and using the dissolved liquid for a food product. The reference does not remotely suggest that the crystals obtained from the fish scales would have use nor does the reference remotely suggest any process which would reduce the odor and maintain the pearlescence of the crystalline material derived from the fish scales. Accordingly, since neither of the applied references singularly or combined are remotely concerned with treating a pigment derived from fish scales with complex metal hydride, how could the references remotely suggest any of the specific ranges which are disclosed. Importantly, the secondary reference is concerned with dissolving the fish scales to form a liquid whereas in the presently claimed invention, the crystalline material is extracted from the fish scales which become the pigment to be treated in the claimed invention. The fact that Applicants have shown that the pigment derived from fish scales can be deodorized is not at all suggested in any of the applied art.

The Examiner states that the extraction of crystalline pigment from fish scales is not recited in the rejected claims. The Examiner further states that although the claims are interpreted in light of the specification, limitations from

the specification are not read into the claims. First, Appellants argue that neither of the applied references are concerned with treating a pigment of any kind. Saiga is concerned with purifying long-chain aliphatic amines derived from fats and oils, and the secondary reference to Hiroshi is concerned with liquefying or dissolving the fish scales for use in a food product. Further, the claimed process of deodorizing "pigment derived from fish scales" as the Examiner says must be interpreted in light of the specification. The specification clearly indicates what is meant by the pigment derived from fish scales and is set forth in the "Background of the Invention" at pages 1 and 2 of the specification and under the "Detailed Description of the Invention" at lines 15-20. Thus, the claimed method of treating pigment "derived from fish scales" clearly is understood to mean guanine crystals extracted from the fish scales, as set forth throughout the specification. Neither of the references again are concerned with treating pigment and certainly not treating guanine crystals extracted from fish scales.

Claims 1 and 18-20 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Saiga in view of Hiroshi in further view of U.S. Patent No. 4,486,334 ("Horiuchi").

Appellants readily admit that cosmetics have been derived from pigments obtained from fish scales prior to the present invention. The problem with such cosmetics is that such cosmetics were provided with an unpleasant odor. The present invention is directed to treating the pigment derived from fish scales to reduce the odor. The combination of Saiga and Hiroshi as discussed above does not remotely suggest treating pigment derived from fish scales with a complex borohydride. While the primary reference teaches chemically treating long-chain aliphatic amines with borohydride compounds, the reference does not remotely suggest treating a pigment, a solid, with such materials, let alone a pigment derived from fish scales. The secondary reference is not concerned with deodorizing the crystalline material (pigment) obtained from fish scales but is concerned with dissolving the fish scales to form a deodorized liquid. The liquid of the secondary reference is used for a

In view of the above remarks, it is believed that claims 1-20 patentably distinguish over the art of record and that the Final Rejection of such claims is improper. Appellants respectfully solicit reversal of the Final Rejection and the allowance of claims 1-20.

Respectfully submitted,

Date: 6/17/2008

A handwritten signature in dark ink, appearing to read "Stuart D. Frenkel", written over a horizontal line.

Stuart D. Frenkel  
Reg. No. 29,500

Frenkel & Associates, P.C.  
3975 University Drive, Suite 330  
Fairfax, VA 22030  
Telephone: (703) 246-9641  
Facsimile: (703) 246-9646

CLAIMS APPENDIX

The claims in this Appeal are:

1. A process for the deodorization of pigment derived from fish scales comprising contacting said pigment with a complex metal hydride.
2. The process of claim 1 wherein said pigment comprises guanine.
3. The process of claim 1 wherein said pigment is in the form of a paste comprising pigment and water when contacted with said complex metal hydride.
4. The process of claim 1 wherein said complex metal hydride is sodium borohydride.
5. The process of claim 1 comprising mixing said complex metal hydride and said pigment to form a mixture and subsequently adding a weak acid to cause foaming of off-gassing from said mixture.
6. The method of claim 5 wherein said complex metal hydride is sodium borohydride.
7. The process of claim 6 wherein said weak acid is an organic acid.
8. The process of claim 7 wherein said organic acid is acetic acid.
9. The process of claim 6 wherein said pigment is in the form of a paste comprising pigment and water, mixing said paste with sodium borohydride to form a mixture, said sodium borohydride being added to said mixture in amounts ranging from 0.5-10 wt% of said pigment paste.
10. The process of claim 9 wherein said sodium borohydride is added as a solid powder.

11. The process of claim 10 wherein said sodium borohydride powder is added in amounts of 1 wt% relative to said pigment paste.
12. The process of claim 9 wherein said weak acid is added in amounts of from about 0.5 to 10 wt% of said pigment paste.
13. The process of claim 12 wherein said weak acid is added in amounts of about 1 wt% relative to said pigment paste.
14. The process of claim 9 wherein said weak acid is added to said mixture of pigment paste and sodium borohydride no more than three hours after said mixture is formed.
15. The process of claim 14 wherein said weak acid is added to said mixture of pigment paste and sodium borohydride less than one hour after said mixture is formed.
16. The process of claim 9 wherein said weak acid is an organic acid.
17. The process of claim 16 wherein said organic acid is acetic acid.
18. A cosmetic formulation containing the pigment treated in accordance with the process of claim 1.
19. A cosmetic formulation containing the pigment treated in accordance with the process of claim 5.
20. A cosmetic formulation containing the pigment treated in accordance with the process of claim 10.



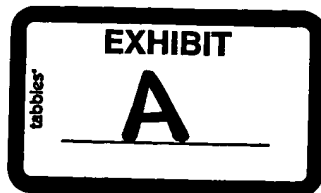
EVIDENCE APPENDIX

Translations of Saiga (A) and Hiroshi (B).

RELATED PROCEEDINGS APPENDIX

U.S. Serial No. 10/908,503, filed May 14, 2005, Appeal No. 2008-2392.

PTO 07-5619



10/747,668

CC=JP DATE=19761222 KIND=A  
PN=51149211

METHOD FOR PURIFYING ALIPHATIC AMINES  
[Shibozoku Amin No Seiseiho]

Daini Saiga, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. July 2007

Translated by: FLS, Inc.

PUBLICATION COUNTRY (19): JP  
DOCUMENT NUMBER (11): 51149211  
DOCUMENT KIND (12): A  
PUBLICATION DATE (43): 19761222  
PUBLICATION DATE (45):  
APPLICATION NUMBER (21): 50073521  
APPLICATION DATE (22): 19750617  
INTERNATIONAL CLASSIFICATION (51): C07C 87/06; C07C 85/26  
DOMESTIC CLASSIFICATION (52):  
INVENTOR (72): SAIGA, DAINI; TOMIDOKORO, SUSUMU;  
INOMIYA, TAKESHI; TAMURA, RIYOUICHI  
APPLICANT (71): THE LION FAT & OIL CO., LTD.  
TITLE (54): METHOD FOR PURIFYING ALIPHATIC  
AMINES  
FOREIGN TITLE [54A]: SHIBOZOKU AMIN NO SEISEIHO

## 1. Title of Invention

Method for Purifying Aliphatic Amines

## 2. Claim(s)

A method for purifying aliphatic amines characterized by adding, as the reducing agent, 0.01 to 2.0% by weight of an alkali metal salt of a borohydride with respect to a long-chain aliphatic amine using a natural fat or oil as the raw material, adding 0.1 to 5.0% by weight of an adsorbent having an alkali adsorption ability with respect to said amine next and at a proportion of at least 20 weight parts to 100 weight parts of said reducing agent.

## 3. Detailed Specifications

The present invention relates to a purification method in which the color tone and odor of long-chain aliphatic amines or and amine compound derivatives thereof manufactured by using a natural fat or oil as the raw material are improved.

In further detail, an improved purification method, wherein a borohydride compound is added to a long-chain aliphatic amine, reduced, and subsequently treated with an adsorbent, whereby the color tone and odor of this amine are improved, and further, the color tone and odor of an amine salt, quaternary ammonium salt, alkyl betaine, alkylene oxide adduct of an amine, and the like derived from this amine are improved, is provided in the present invention.

Aliphatic amines and their derivatives can be applied to diverse

---

\* Numbers in the margin indicate pagination in the foreign text.

fields—from industrial products, such as fiber treatment agents, antistatic agents and emulsifiers, to cosmetics.

However, there are drawbacks because the odor of these aliphatic amines and their derivatives are extremely strong and the color tone is poor; hence, an improvement in these drawbacks has been demanded in the above-mentioned applications, and in particular, the cosmetics field.

A method in which an amine is purified with a borohydride compound to prevent an amine salt, quaternary ammonium salt or alkyl betaine derived therefrom from being colored is disclosed in Tokkai No. 49-95907 as a method of improvement thereof.

In this method, although the decoloring effect on amines is recognized definitely, no deodorizing effect is recognized at all. Moreover, boron oxide, which is a decomposition product of a borohydride compound, remains and this boron compound residue acts as an oxidization reaction catalyst when a derivative of the amine thereof, and in particular, a derivative obtained via a high-temperature reaction, such as an alkylene oxide /2 addition reaction or quaternary ammoniation reaction, undergoes a high-temperature reaction. The product degrades and the amount of odor constituent increases; hence, there is a drawback because the odor is extremely bad.

Oxidizable impurities, such as aldehydes and ketones, are contained in aliphatic amines using natural fats and oils as raw materials. They are odor sources or coloring precursors; hence, a long-chain aliphatic amine using a natural fat or oil as the raw material is more important in a method for solving coloring and odor problems than in the case of

an aliphatic amine using a petroleum product as the raw material.

Furthermore, an aliphatic amine increases the amount of the same oxidizable impurities causing oxidative degradation over time.

Consequently, the oxidizable impurities contained in the aliphatic amines must be removed, but it is necessary to remove the substances that will induce or promote an oxidation reaction.

As a result of painstaking research and investigations to solve these drawbacks, in view of the above problems, the inventors of the present invention discovered that there were remarkable advantages in improving color tone and odor by acting a borohydride alkali metal salt on a long-chain aliphatic amine using a natural oil or fat as the raw material and adsorbing it next with an adsorbent having alkali adsorption ability, which led them to completing the present invention.

That is, the present invention is a method for purifying aliphatic amines in which 0.01 to 2.0% by weight of an alkali metal salt of a borohydride with respect to a long-chain aliphatic amine are added as the reducing agent, a natural fat or oil is used as the raw material, 0.1 to 5.0% by weight of an adsorbent having an alkali adsorption ability with respect to said amine and at a proportion of at least 20 weight parts to 100 weight parts of said reducing agent are added next.

The amine which can be applied to the purification method of the present invention is an aliphatic amine using a natural fat or oil as a raw material, and in particular, an aliphatic amine having at least one alkyl group having eight or more carbons.

Especially effective amines include monoalkylamines,

aminopropylmonoalkylamines, monoalkyldiethylamines, monoalkyl-N,N-dihydroxyethylamines, dialkylamines and dialkylmonomethylamines.

Although a borohydride alkali metal salt selected from among sodium borohydride, potassium borohydride and lithium borohydride may be used for the borohydride compound of the present invention, on the contrary the advantages of the present invention cannot be obtained with hypophosphorous acid, hypophosphoric acid, sodium sulfite, hydrazines, etc.

The amount of the borohydride alkali metal salt used varies strictly depending on the type, attributes and treatment conditions of the amines. It ranges from 0.01 to 2.0% by weight (referred to as "%" hereinafter unless otherwise noted), and preferably, from 0.1 to 1.0% to the amine.

When it is less than the lower limit of 0.01%, there are few decoloring and deodorizing effects and the object of the present invention cannot be achieved.

And when it is greater than the upper limit of 2.0%, there is little improvement in the effect upon increasing the amount of use. When the amount used is extremely high, the borohydride compound of the reducing agent or its decomposition product is not removed sufficiently in the adsorption treatment performed next; hence, the treatment effects may be diminished.

An adsorbent having an alkali adsorption ability is used for the adsorbent used in the present invention, and in particular, silica, alumina, sodium oxide, magnesium oxide, and the like are preferred.



It is necessary to satisfy both of the conditions that the amount of this adsorbent used is 0.1 to 5.0%, and preferably, 0.5 to 2.0% with respect to the amine, and the ratio of 20 weight parts (simply referred to as "parts" hereinafter) or more to 100 parts of the above-mentioned reducing agent.

In this case, if the proportion of the adsorbent to the reducing agent is less than 20 parts of adsorbent to 100 parts of reducing agent, the synergistic effects of this adsorbent and reducing agent decline sharply.

Moreover, it is industrially uneconomical and unsuitable when the amount of the adsorbent used is less than 0.1% because the deodorizing effect is reduced by half, or when it exceeds 5.0% because an improvement in the treatment effects proportional to the increase in the amount added is not recognized.

Although the method for purifying an aliphatic amine of the present invention comprises both a reducing treatment step in which the borohydride alkali metal salt is added to the aforesaid amine first and an adsorption treatment step in which the adsorbent having an alkali adsorption /3 ability is added next, a high-temperature, long-term treatment greater than necessary should be avoided for the purpose of preventing the thermal degradation of the amine at the respective conditions of these treatments. As a consequence, the respective treatment conditions vary depending on the type of amine, but generally it is favorable to treat it at 30 to 100°C, and preferably, 50 to 80°C for 15 minutes to about 3 hours.

In a specific method of the present invention, the amine is accommodated in a container having a heating device and a stirring device, the borohydride

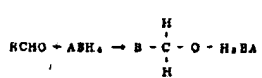
alkali metal salt is added thereto and reduced at the aforesaid treatment conditions in a nitrogen atmosphere, the aforesaid adsorbent having alkali adsorption ability is added next and stirred, normally for about 30 minutes to 1 hour and 30 minutes, cooled, subsequently filtered to separate and remove the borohydride alkali metal salt, adsorbent, and the like and obtain a purified amine.

In the aliphatic amine purified in the purification method of the present invention described in detail above, a more superior purified amine with improved color tone and odor can be obtained more easily and quickly than in a conventional method, as made clear from the practical examples and the like below.

Furthermore, the color tone and odor of the derivatives, such as amine salts and quaternary ammonium salts, derived from these aliphatic amines may be improved in the same way as well, and outstanding commodities, such as fiber treatment agents, antistatic agents, emulsifiers and beauty products, are obtained, unlike in the past.

Although the reasons the present invention provides such outstanding effects are not clear, they are inferred as follows.

That is, although large amounts of oxidizable impurities, such as aldehydes and ketones, are contained in the aliphatic amines using natural fats and oils, esters are produced by a reaction between these impurities and the borohydride alkali metal salt in accordance with the reaction formula shown next.

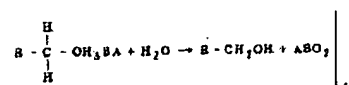


(providing A in the above formula is an alkali metal and B is an aliphatic

alkyl group).

When the adsorbent having alkali adsorption ability is used because the ester of the reaction product on the right side has an alkaline active group, the effects thereof are remarkable.

In addition, although this ester reacts with the moisture in the amine according to the following formula:



metaboric acid ions are generated and are dissolved in the amine as a source of coloring in the quaternizing reaction and the like of the amine, and the metaboric acid side reaction product ions ( $\text{BO}_2^-$ ) also can be adsorbed and removed altogether.

That is, although just a borohydride compound ~~is used as the~~ reducing agent in the reducing treatment method used in a conventionally-known method for purifying an aliphatic amine, the borohydride compound in the method of the present invention adsorbs the impurities and has an effect for converting them intermediates that are more readily adhered adsorbed.

The present invention is described further next along with the test examples, practical examples, comparative examples, etc.

#### Test Examples

Comparison tests on the improvements in color tone and odor by the reduction-adsorption treatment of the method of the present invention and a conventionally-known adsorption-only treatment was performed by using distearylamine manufactured from a natural fat or oil raw material (97.3% pure amine) as the sample, selecting the reducing agent, sodium borohydride, and using "Kyoward 600S" (trade name, made by Kyowa Chemical

Industry Co., Ltd., 2 MgO·6 SiO<sub>2</sub>·x H<sub>2</sub>O) as the adsorbent.

These treatment effects were evaluated with an amine and a quaternary ammonium salt.

The color tone evaluation was performed using a Gardner-Hellige Colorimeter, and small numerals reflect outstanding decoloring effects.

Moreover, twenty specially trained test subjects were selected for the purpose of judging odors who provided their services at the workplace of an inventor of the present invention, to find how many (x) of the twenty subjects perceived the odor improving effects thereof according to the math expression: x subjects/20 subjects. As a consequence, in an example in which, e.g., 1/20 is an example of poor deodorizability, while 20/20 is an example of outstanding deodorization, showing that all twenty subjects could sense a deodorizing effect.

Table 1

/4

試料番号		1A	2A	3A	4A	5A	6A	7A	8A
試料 の 色 調	色度 (L)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	色度 (a)	0.00	0.05	0.1	0.3	0.5	1.0	3.0	5.0
	色度 (b)	1*	1*	1*	1*	1*	1*	1*	1*
	色度 (c)	5/20	11/20	15/20	17/20	19/20	20/20	20/20	20/20
(A)	試料番号	2	2	2	2	2	2	2	2
	色度 (L)	2/20	7/20	12/20	17/20	20/20	20/20	20/20	20/20
	色度 (a)	2	2	2	2	2	2	2	2
	色度 (b)	0/20	0/20	1/20	2/20	4/20	5/20	5/20	5/20
試料 の 色 調	色度 (L)	3	3	3	3	3	3	3	3
	色度 (a)	0/20	0/20	0/20	3/20	5/20	6/20	7/20	7/20
	色度 (b)	3	3	3	3	3	3	3	3
	色度 (c)	0/20	0/20	0/20	3/20	5/20	6/20	7/20	7/20

Key:

Reduction-Adsorption Treatment Method (A)	Test No.			
	Treatment	Reducing Agent (%)		
		Adsorbent (%)		
	Evaluation of Results	Treatment evaluation of amine sample	Decoloring	
			Deodorization	
		Quaternary Salt Sample Treatment Evaluation	Decoloring	
Deodorization				
Adsorption Treatment Method Only (B)	Test No.			
	Treatment	Reducing Agent (%)		
		Adsorbent (%)		
	Evaluation of Results	Treatment evaluation of amine sample	Decoloring	
			Deodorization	
		Quaternary Salt Sample Treatment Evaluation	Decoloring	
			Deodorization	

Notes: (1) The ■ symbol denotes a comparative example. (2) The adsorption treatment method (B) naturally is related to the comparative examples.

As is well understood from Table 1, it is easily clarified that the reduction-adsorption treatment method is outstanding. For example, in test no. 3A, it is  $\frac{0.1}{0.5} \times 100 = 20\%$  since 0.5% of the reducing agent and 0.1% of the adsorbent are used. In the post-treatment evaluations, satisfying the conditions of the present invention also is outstanding.

It is well understood that the reduction-adsorption treatment method of the present invention is far more superior than the conventional adsorption treatment-only method.

Moreover, in test no. 1A of the reduction-adsorption treatment method in Table 1, no (0.00%) adsorbent was added at all and 0.5% reducing agent was added; hence, there is no effect by an adsorbent. At that time, the deodorizing effect of the quaternary ammonium salt is 2/20, and only the effect of the reducing agent can be seen by the "2" in the numerator thereof.

The treatment effects on this quaternary ammonium salt and the reduction-adsorption treatment method and adsorption treatment method

are illustrated as in the appended graph.

That is, curve A in the graph shows test nos. 1A to 8A in Table 1 and curve B shows 1B to 8B in Table 1 plotted as a curve; hence, when there is no adsorbent at all (point 1A), deodorizing is 2/20. Therefore, the deodorizing evaluation value x shown by the difference between at least curves comprising curve C using this as the starting point, point D and curve B and curve A indicates the synergistic effects of the reducing agent and adsorbent on curve A.

It is well understood that there is a sufficient effect when the amount of the adsorbent in the reduction-adsorption treatment method is about 0.3%, and that 1.0% or more approaches a constant value in terms of the effect thereof.

According to this practical example, the relationship between the constitution and advantages of the present invention may be clearly understood.

The practical examples and comparative examples are further described next.

#### Practical Examples and Comparative Examples

Comparative examples in which various amines are used as samples, and one of the reducing agent or the adsorbent used in the present invention is used and practical examples in which the treatment was performed by using both of these agents are shown below.

The methods for evaluating the color tone, odor, and the like in /5 each of these examples employed the same methods as in the aforementioned practical examples.

Moreover, a sample, which is a solid at room temperature, such as distearylamine, is coated on a 7 cm diameter filter paper, and moreover, contains a solvent, such as a quaternary ammonium salt, is evaluated after drying it for 10 minutes to remove the solvent.

In addition, a sample that is a liquid at room temperature, such as monoalkyldimethylamine, is evaluated after immersing a 7 cm diameter filter paper therein for 2 minutes and removing it.

#### Comparative Examples

A flask was charged with 500 g distearylmonomethylamine (98.6% pure amine) and heated to 75°C in a nitrogen atmosphere to dissolve the amine.

Next, 2.5 g sodium borohydride is added and subjected to a stirring and reducing treatment for 1 hour in a nitrogen atmosphere.

5.0 g of adsorbent were added thereto, treated for 0.5 hours at the same conditions as in the reducing treatment, a hot filtration (75°C) is performed using a Hyflo Super-Cel (trade name of filtration aid composed mainly of diatomaceous earth made by Johns-Manville Corp.) to remove the adsorbent, etc.

Quaternization is performed using this treated amine, and the color tone and odor are evaluated with amines and quaternary ammonium salt. The results obtained when the adsorption-treated amines and reduced amines with various adsorbents were used are compared and shown in Table 2.

Moreover, the treatment method of the adsorption-treated amine in this comparative example is performed under the same conditions as those of the adsorption treatment in the case of the above-mentioned practical examples. The adsorbent is removed by filtration to obtain an

adsorption-treated amine, and moreover, the treatment for reducing the reduced amine is the same as that in the practical examples.

Table 2

比較試験番号	1	2	3	4
処理剤	還元剤	還元剤	還元剤	還元剤
還元剤	—	S.B.H.	P.B.H.	S.B.H.
吸着剤	2MgO Kyoward 600S	—	—	—
試験711 脱色	2	1	2	2
脱色評価 結果	3/20	2/20	1/20	1/20
試験712 脱色	2	1	2	2
脱色評価 結果	4/20	2/20	2/20	1/20

Key:

Comparative Example Test No.				
Treatment Method		Adsorption Method	Reducing Method	Reducing Method
Reducing Agent				
Adsorbent				
Amine Sample Treatment Evaluation	Decoloring			
	Deodorization			
Quaternary Salt Sample Treatment Evaluation	Decoloring			
	Deodorization			

(Notes) S.B.H.: sodium borohydride; P.B.H.: potassium borohydride; ®: "Kyoward 600S" (trade name, made by Kyowa Chemical Industry Co., Ltd.)

Moreover, the methods for evaluating the decoloring and decolorization were performed using the same methods as in the practical examples (including the below-mentioned practical examples).

When the reducing agent and adsorbent are not used together as such, the effects are extremely low even when a definite % of each of these individual agents according to the present invention is added individually.

In addition, if the alkali of the borohydride is a sodium salt or potassium salt, the treatment effects thereof remain wholly unchanged.

#### Practical Example 1

Monostearyl dimethylamine (97.5% pure amine) manufactured by using



a natural fat or oil as the raw material was used as the sample.

Although the amount of the sodium borohydride used as the reducing agent was 0.5% respect to the amine, and moreover, the amount of the adsorbent used was 1.0%, the various types thereof changed.

Moreover, the adsorbents include "Kyoward #600S" (see Table 2), "Kyoward #700" ( $\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ), "Kyoward #400" ( $\text{Na}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ), "Kyoward #500" ( $6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) (all trade names of Kyowa Chemical Industry Co., Ltd.), etc.

These test results have been shown in Table 3.

Table 3

/6

試料	比較例	実施例	比較例	実施例	比較例	実施例
番号	1	2	3	4	5	6
乳油の含有率	—	—	—	—	—	—
還元剤	—	—	—	—	—	—
吸着剤	—	—	—	—	—	—
試料の色	1	1	1	1	1	1
試料の臭気	1	1	1	1	1	1
試料の脱色	1	1	1	1	1	1
試料の脱臭	1	1	1	1	1	1

Key:

Test No.		Comparative Example		Practical Example			
Treatment Method		Adsorption Method		Reduction-Adsorption Method (Method Of Practical Example)			
Reducing Agent							
Adsorbent							
Amine Sample Treatment Evaluation	Decoloring						
	Deodorization						
Quaternary Salt Sample Treatment Evaluation	Decoloring						
	Deodorization						

Substantially the same outstanding decoloring and deodorizing results were obtained even when the type of adsorbent was replaced, as shown in Table 3. It is clear that the results of the comparative examples are inferior.

## Practical Example 2

This example was carried out with various amines using natural fats and oils as raw materials. The results in Table 4 were obtained next.

Moreover, sodium borohydride was used as the reducing agent, and the amount thereof used was 0.5% with respect to the amine, while 1.0% of the aforesaid "#600S," with respect to the amine, was used for the adsorbent.

Moreover, the names of the amines and the purities thereof are as shown in the table.

Table 4

試験番号	1	2	3	4	5
モノステアリン酸	モノステアリン酸	モノステアリン酸	モノステアリン酸	モノステアリン酸	モノステアリン酸
アミノエチルモノステアリン酸	アミノエチルモノステアリン酸	アミノエチルモノステアリン酸	アミノエチルモノステアリン酸	アミノエチルモノステアリン酸	アミノエチルモノステアリン酸
(純度)	(99.2%)	(99.0%)	(97.3%)	(98.6%)	(98.2%)
モノステアリン酸	1	3	1	1	2
アミノエチルモノステアリン酸	20/20	19/20	19/20	17/20	19/20
ジステアリン酸	1	3	1	1	2
アミノエチルジステアリン酸	20/20	20/20	20/20	18/20	17/20

Key:

Test No.		Monostearyl amine	Aminoethyl-monostearyl amine	Distearyl amine	Distearyl-monostearyl amine	Monostearyl-N,N-di-hydroxy-ethylamine
Type of amine sample						
(Purity)						
Amine Sample	Decoloring					
Treatment	Deodorization					
Evaluation						
Quaternary Salt Sample	Decoloring					
Treatment	Deodorization					
Evaluation						

It is clear from Table 4 that the treatment in the method of the present invention is extremely outstanding.

## Practical Example 3

The present invention was carried out by changing the type of the

various amine derivatives using natural oils and fats as raw materials.

Moreover, sodium borohydride is used as the reducing agent, while the amount thereof used is 0.5% with respect to the amine. The aforesaid "#600S" is used as the adsorbent, while the amount thereof used is 1.0% with respect to the amine.

Furthermore, comparative examples were described for comparing some samples.

Table 5

試験番号	比較例		実施例						
	1	2	3	4	5	6	7	8	9
製造法	還元法	鉄屑法	還元- 過酸化	同左	同左	同左	同左	同左	同左
試料アミン の種類	モノスタ リルジメ チルアミ ン	同左	モノスタ リルジメ チルアミ ン	同左	モノスタ リルジメ チルアミ ン	同左	ジスタ リルモノ メチルア ミン	同左	モノスタ リルジメ チルアミ ン
(純度%)	(97.5)	(97.5)	(98.2)	(99.2)	(97.5)	(97.5)	(98.6)	(98.6)	(97.5)
溶媒の 種類	四級塩	同左	同左	PO付 加体	アルキル ペタイン	脂肪 塩	四級塩	アルキル ペタイン	四級塩
結晶性	2	3	1	2	1+	2	1	1+	1
結晶性試験	3/20	4/20	19/20	20/20	18/20	20/20	20/20	18/20	20/20

Key:

Test No.	Comparative Example		Practical Example						
Treatment Method	Reducing method	Adsorption method	Reduction-Adsorption Method (Method of Practical Examples)	Same as at left	Same as at left	Same as at left	Same as at left	Same as at left	Same as at left
Type of Amine Sample  (% purity)	Mono-stearyl dimethylamine	Same as at left	Mono-stearylamine	Same as at left	Mono-stearyl dimethylamine	Same as at left	Distearylmonomethylamine	Same as at left	Mono-stearyl dimethylamine
Type of Derivative	Quaternary salt	Same as at left	Same as at left	FO additive	Alkyl betaine	Fatty acid salt	Quaternary salt	Alkyl betaine	Hydrochloride
Derivative	Decoloring								
Treatment Evaluation	Deodorization								

It is evident from Table 5 that the practical examples of the present invention are outstanding. /7

#### Practical Example 4

A case in which the amount of adsorbent is changed is shown next.

In this case, sodium borohydride was used for the reducing agent, the amount thereof used was 1.0% with respect to the amine, while "Kyoward #600S" ( $2 \text{ MgO} \cdot 6 \text{ SiO}_2 \cdot x \text{ H}_2\text{O}$ ) was used for the adsorbent.

In addition, the residual boron compound left in the treated amine was determined. A determination test using a coloring method with turmeric test paper was performed for the test method thereof by charging a reactor comprising a glass flask with 400 g of the respective treated amines,

and further, adding 100 g of warm water and stirring this for 1 hour at 75°C, letting it stand still to separate into layers, and separating out the bottom aqueous layer.

Moreover, the numerals shown by the items of this determination test indicated the magnification factors after separation of the aqueous layer, and in this case, at what magnification a turmeric coloring reaction was not observed when the boron aqueous solution was diluted.

The amine used in this practical example is distearylamine (97.3% amine).

Table 6 shows the evaluation results when the amount of adsorbent used is changed and the determination results of the boron compound using the turmeric test paper.

Table 6

実験番号	1	2	3	4	5	6	7
吸着剤使用量g	0.02 <sup>a</sup>	0.05 <sup>a</sup>	1.0	3.0	5.0	7.0 <sup>a</sup>	10.0 <sup>a</sup>
処理アミン脱色	1*	1	1	1	1	1	1
の評價結果	5/20	11/20	16/20	20/20	19/20	18/20	20/20
吸着剤脱色	1	1	1	1	1	1	1
の評價結果	5/20	7/20	15/20	20/20	19/20	20/20	18/20
吸着剤の定数	120	15	3	2	1.5	1.5	1.5

Key:

Test No.		
Amount of Adsorbent Used (%)		
Amine Sample Treatment Evaluation	Decoloring	
	Deodorization	
Quaternary Salt Sample Treatment Evaluation	Decoloring	
	Deodorization	
Boron Determination		

(Notes) The \* symbol denotes a comparative example.

#### Practical Example 5

The results upon changing the amount of reducing agent are shown

next.

Moreover, sodium borohydride is used for the reducing agent, while "Kyoward #600S" is used for the adsorbent and the amount thereof used is 2.0% with respect to the amine. In addition, the amine used at this time is distearylamine (97.3% amine). The results of this test are as shown in Figure 7.

Table 7

実験番号	1	2	3	4	5	6	7
還元剤使用量	0.005 <sup>a</sup>	0.01	0.1	0.5	2.0	4.0 <sup>a</sup>	6.0 <sup>a</sup>
吸着剤の脱色	2	1	1	1	1	1	1
の試験結果	4/20	12/20	18/20	17/20	20/20	19/20	20/20
結果の脱色	2	1	1 <sup>a</sup>	1	1	1	1
の試験結果	2/20	11/20	20/20	18/20	20/20	20/20	18/20

Key:

Test No.		
Amount of Reducing Agent Used (%)		
Amine Sample Treatment Evaluation	Decoloring	
	Deodorization	
Quaternary Salt Sample Treatment Evaluation	Decoloring	
	Deodorization	
Boron Determination		

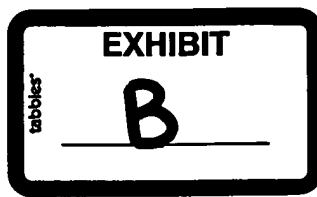
(Notes) The <sup>a</sup> symbol denotes a comparative example.

It is evident from Table 7 that the purification method of the present invention is outstanding.

#### 4. Brief Description of the Drawings

The drawing is a graph showing the synergistic effects of the present invention upon comparing the evaluations of the reduction-adsorption treatment method in a number of examples of embodiments of the present invention and a conventional adsorption treatment method using a deodorization evaluation value x typically using a quaternary amine in the test.

PTO 07-5620



CC=JP DATE=20030325 KIND=A  
PN=15088337

10/747,668

FISH SCALE LIQUID, PRODUCTION METHOD FOR FISH SCALE LIQUID,  
PROCESSED FOOD, AND PRODUCTION METHOD FOR PROCESSED FOOD  
[Gyorin'eki, Gyorin'eki No Seizo Hoho, Kako Shokuhin  
Oyobi Kako Shokuhin No Seizo Hoho]

Hiroshi Nagasaki

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C.

July 2007

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	2003088337
DOCUMENT KIND	(12):	A
	(13):	PUBLISHED UNEXAMINED APPLICATION (Kokai)
PUBLICATION DATE	(43):	20030325
PUBLICATION DATE	(45):	
APPLICATION NUMBER	(21):	2001282998
APPLICATION DATE	(22):	20010918
INTERNATIONAL CLASSIFICATION	(51):	A23L 1/325, 1/30
INVENTOR	(72):	NAGASAKI, HIROSHI
APPLICANT	(71):	ORGANO CORPORATION
TITLE	(54):	FISH SCALE LIQUID, PRODUCTION METHOD FOR FISH SCALE LIQUID, PROCESSED FOOD, AND PRODUCTION METHOD FOR PROCESSED FOOD
FOREIGN TITLE	[54A]:	Gyorin'eki, Gyorin'eki No Seizo Hoho, Kako Shokuhin, Oyobi Kako Shokuhin No Seizo Hoho



[Claim 1] A fish scale liquid that is acidic water in which fish scales are dissolved or dispersed.

[Claim 2] A process for preparing a fish scale liquid by dissolving or dispersing fish scales in acidic water.

[Claim 3] A process for producing the fish scale liquid stated in Claim 1, wherein the aforesaid acidic water is acidic water having a pH of 5 or lower.

[Claim 4] The process for producing a fish scale liquid stated in Claim 2 or 3, wherein the acid in the aforesaid acidic water is citric acid or phosphoric acid.

[Claim 5] The process for producing a fish scale liquid stated in any one of Claims 2 through 4, wherein fish scales are dissolved or dispersed in an acidic water in the presence of cyclodextrin.

[Claim 6] Processed food that contains the fish scale liquid stated in Claim 1.

[Claim 7] A method for preparing processed food by adding the fish scale liquid stated in Claim 1.

---

\* Number in the margin indicates pagination in the foreign text.

[Detailed Description of the Invention]

[0001] [Technical Field of the Invention]

The present invention pertains to a fish scale liquid, production method for the fish scale liquid, processed food containing the fish scale liquid, and production method for said processed food.

[0002] [Prior Art]

In processing fish caught by fishing, such as sardines and so forth, scales (hereinafter referred to as "fish scales") are generated as byproducts in large quantities. Fish scales generated in fishery processing had been disposed of as industrial wastes for many years due to lack of useful applications. In recent years, however, since fish scales contain collagen, calcium, and the like, they have been drawing attention as another nutrient material and the like.

[0003] As new applications of fish scales, anti-osteoporosis drugs (JP-A-H10-203995), agents for improving the luster of animal coats (JP-A-H10-155428), and so forth are known. As fish scales for food product use, fish scale powders obtained by pulverizing fish scales into a powder form are known.

[0004] Fish scales that are simply powdered, however, do not dissolve in ordinary water; therefore, when fish scale powder is added to water, it ends up precipitating. For this reason, it is difficult to use fish scales for beverages or jelly, and it has not been

possible to effectively utilize the nutritional constituents that fish scales possess.

[0005] Furthermore, fish scales have a distinctive odor (hereinafter referred to as "fish scale odor"), and the amount of fish scales that can be added to food products has been extremely small.

[0006] [Objective that the Invention Intends to Achieve]

The objective that the invention intends to achieve is to provide a fish scale liquid that is prepared from heretofore-discarded fish scales as the raw material, that is readily applicable to food products, and that is odorless and also to provide a production method for it, processed food containing said fish scale liquid, and a production method for said processed food.

[0007] [Means For Solving The Problems]

The present inventor researched extensively to achieve the aforesaid objective and, as a result, learned that fish scales dissolve in acidic water and also that this fish scale solution has a considerably reduced fish odor. Based on these findings, the present invention was achieved.

[0008] That is, the first invention for achieving the aforesaid objective pertains to a fish scale liquid that is acidic water in which fish scales are dissolved or dispersed.

[0009] The second invention for achieving the aforesaid objective pertains to a process for producing a fish scale liquid by dissolving or dispersing fish scales in acidic water.

[0010] The third invention for achieving the aforesaid objective is the aforesaid second invention, in which the aforesaid acidic water is acidic water having a pH of 5 or lower.

[0011] The fourth invention for achieving the aforesaid objective is the aforesaid second or third invention, in which the acid in the aforesaid acidic water is citric acid or phosphoric acid.

[0012] The fifth invention for achieving the aforesaid objective is the aforesaid second to fourth inventions, in which fish scales are dissolved or dispersed in acidic water in the presence of cyclodextrin.

[0013] The sixth invention for achieving the aforesaid objective pertains to processed food that contains the fish scale liquid of the aforesaid first invention.

[0014] The seventh invention for achieving the aforesaid objective pertains to a process for producing processed food by adding the fish scale liquid of the aforesaid first invention.

[0015] [Preferred Mode of the Invention]

No specific limitations are imposed on the type of fish from which the fish scales used in the present invention are obtained as long as they are fish scales that are byproducts of fishery processing, and, some examples of the fish include sardines, saury, and the like,

which are caught in large quantities. The fish scales separated from the fish bodies in fishery processing are washed with water and used as the raw material fish scales.

[0016] In order to produce the fish scale liquid of the present invention, the aforesaid fish scales are dissolved or dispersed in acidic water, but, for the purpose of shortening the dissolving time, it is desirable to pulverize the fish scales by known pulverization means. Examples of the pulverization means include a hammer mill, ball mill, pin mill, jet mill, atomizer, pulverizer, and so forth.

[0017] To produce the fish scale liquid of the present invention, fish scales are added in a concentration of 0.1 to 3 % by weight to acidic water whose pH has been adjusted to 5 or lower, preferably from 4 to 1.5, and agitated, thereby dispersing or dissolving them uniformly. The obtained fish scale liquid has a greatly reduced fish scale odor.

[0018] In the fish scale liquid of the present invention, fish scales are dissolved completely when the concentration of the fish scales is low. When the concentration of the fish scales is high, however, there are some fish scales that cannot be dissolved completely and remain in a dispersed state in the dissolved fish scales, but they do not precipitate.

[0019] No specific limitations are imposed on the acid used for producing the acidic water of the present invention, and any acid that

can be used for food products may be used, some examples of which /3  
include organic acids, such as citric acid, lactic acid, malic acid,  
and the like, and inorganic acids, such as phosphoric acid,  
hydrochloric acid, and the like, of which citric acid or phosphoric  
acid is preferably used owing to their strong dissolving and  
dispersing power on fish scales.

[0020] The fish scale liquid of the present invention may be  
produced by preparing acidic water beforehand and then adding fish  
scales to this acidic water, by adding fish scales and an acid  
simultaneously, or by dispersing fish scales in water and subsequently  
adding an acid therein.

[0021] Furthermore, the concomitant use of cyclodextrin can  
improve the deodorization of fish scale odor. Examples of the  
cyclodextrin used here include  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin, and  $\gamma$ -  
cyclodextrin.

[0022] Cyclodextrin should be added in a concentration at which  
it does not precipitate at ordinary temperature, and the concentration  
for  $\alpha$ - and  $\gamma$ -types is selected from a range of 10 % or less and 2 % or  
less for  $\beta$ -type.

[0023] It has not been elucidated why dissolving fish scales in  
acidic water deodorizes fish scales, but the reduction of fish scale  
odor by the concomitant use of cyclodextrin is believed to be achieved  
by the capturing of odorants inside circular-form cyclodextrin.

[0024] Since the fish scale liquid of the present invention has a dramatically reduced fish scale odor and is a stable solution, it can be applied to various kinds of processed food products. There are no limitations imposed on processed food products to which the fish scale liquid of the present invention can be added as long as they are food products of pH 5 or lower, and some examples include such processed food as juice, energy drinks, soup, jelly, terrines, puddings, mayonnaise, yogurt, jams, snacks, seasonings, and so forth.

[0025] To confect the processed food of the present invention, ingredients, such as sugar, artificial sweeteners, gelling agents, seasonings, colorants, spices, and so forth, for the processed food are selected and used as appropriate according to the type of the processed food.

[0026] To produce the processed food of the present invention, the fish scale liquid of the present invention is added in the production process of the processed food. More specifically, in the case of producing jelly, fish scales are placed and stirred well in water to which an acidic substance, such as citric acid or the like, and cyclodextrin have been added, thereby dissolving the fish scales, and the solution is heated to 60 °C. Separately, a solution is prepared by dissolving a gelling agent and kept at 70 °C, and both solutions are mixed thoroughly. The resulting liquid is filled in containers and sealed and subsequently cooled, thereby obtaining jelly.

[0027] In the case of producing a beverage, fish scales are placed and stirred well in water to which an acidic substance, such as citric acid or the like, and cyclodextrin have been added, thereby dissolving the fish scales, and the solution is heated to 60 °C. To this solution, sugar, spices, colorants, and so forth are added and stirred to homogenize it, and the resulting liquid is packed in containers and sealed, thereby obtaining a beverage.

[0028] [Working Examples]

Working Examples 1 through 5 and Comparative Example 1

According to the compositional ratios shown in Table 1, fish scale powder (product name "Collagetide," a product of Shinda Kanzume Co.), sugar,  $\beta$ -cyclodextrin, and citric acid (or lactic acid) were added in water and heated, thereby preparing a fish scale liquid. This liquid was cooled and subsequently evaluated. The procedures performed were as follows.

<Procedures> 1)

To water, fish scale powder, sugar, citric acid (or lactic acid), and  $\beta$ -cyclodextrin were added.

[0029] 2} The mixture was stirred for 5 minutes at 9000 rpm with a mixer (product name "Clearmix CLM-L2.5S," a product of M Technique Co.)

[0030] 3) The liquid obtained in 2 was heated to 85 °C.



[0031] The liquid obtained in 3 was cooled and subjected to organoleptic evaluation.

<Evaluation criteria>

Dispersibility · Solubility ○: Dispersed or dissolved.

[0032] △: Slight formation of precipitation, which could be dispersed easily with light stirring.

[0033] X: Not completely dispersed and dissolved.

Fish scale odor ○: No odor when compared with the control group.

[0034] △: Slight odor when compared with the control group.

[0035] X: Bad odor when compared with the control group.

[0036] [Table 1]

	対照区	実施例1	実施例2	実施例3	実施例4	実施例5	比較例1
魚鱗粉末(d)	(a)	3 (b)	3 (b)	5 (b)	5 (b)	3 (b)	0.5 (c)
砂糖 (e)	15	15	15	15	15	15	15
クエン酸 (f)	0.36	0.36	0.36	0.36	0.36	—	—
50 %乳酸溶液 (g)	—	—	—	—	—	4	—
β-サイクロデキストリン (h)	—	—	2	—	2	2	—
水 (i)	84.64	81.64	79.64	79.64	77.64	76	84.5
合計 (j)	100	100	100	100	100	100	100
pH	3.6	3.8	3.8	3.9	3.9	3.5	6.9
分散・溶解性 (k)	—	○	○	△	△	○	×
魚鱗臭の有無 (l)	—	○	○	△	○	○	×

Key: a) control group b) working example; c) comparative example; d) fish scale powder; e) sugar; f) citric acid; g) 50 % lactic acid solution; h) β-cyclodextrin; i) water; j) total; k) dispersibility · solubility; l) presence or absence of fish scale odor.

[0037] "Dispersibility · Solubility" Working Examples 1 and 2 were 1/4 completely dispersed and dissolved, and the resulting solutions had a green color.

[0038] Working Examples 3 through 5 precipitated when left standing still, but the precipitate could be dispersed easily with light stirring.

[0039] Comparative Examples 1 and 2 [sic] formed precipitates, and, even when they were stirred, they precipitated again immediately. "Fish scale odor" Working Examples 1, 2, and 4 were compared with the control group and found to have no fish scale odor.

[0040] Working Example 3 had a slight fish scale odor when compared with the control group.

[0041] Comparative Examples 1 and 2 had a definite fish scale odor.

#### Working Example 6

According to the composition shown in Table 2, citric acid, fish scale powder, sugar,  $\beta$ -cyclodextrin, and gelling agents (gellan gum and xanthan gum) were added to water, and the mixture was heated and then cooled, thereby preparing jelly, which was then evaluated. The procedures performed were as follows.

#### <Procedures>

1) To half of the water to be used for making jelly were added fish scale powder, sugar, citric acid, and  $\beta$ -cyclodextrin.

[0042] 2) The mixture was stirred for 5 minutes at 9000 rpm with a mixer (product name "Clearmix CLM-L2.5S," a product of M Technique Co.)

[0043] 3) To the remaining half of the water were added gellan gum and xanthan gum, and the mixture was heated to 90 °C.

[0044] 4) The liquids obtained in 1 and 3 were mixed and subsequently cooled, and the resulting product was subjected to organoleptic evaluation in accordance with the method in Working Example 1. The gel strength was measured with "Rheometer CR-200D" (a product of Sun Kagaku Co.) The measurement was taken with a 5 mm-diameter plunger and at a plunger speed of 60 mm/min.

[0045] [Table 2]

	実施例8 (a)
ジェランガム (b)	0.2
キサンタンガム (c)	0.4
魚鱗粉末 (d)	1
砂糖 (e)	15
クエン酸 (f)	0.35
β-サイクロデキストリン (g)	2
水 (h)	81.64
合計 (i)	100
pH	3.8
分散・溶解性 (j)	○
魚鱗臭の有無 (k)	○
ゲル強度 (g/cm <sup>2</sup> ) (l)	52

Key: a) working example 6; b) gellan gum; c) xanthan gum; d) fish scale powder; e) sugar; f) citric acid; g) β-cyclodextrin; h) water; i) total; j) dispersibility · solubility; k) presence or absence of fish scale odor; l) gel strength.

[0046] In the jelly prepared in Working Example 6, the fish scales were uniformly dispersed, and it did not have a fish scale odor.

[0047] [Effects of the Invention]

The present invention described in Claim 1 provides a fish scale material that can be applied to processed food easily and that has no odor.

[0048] With the inventions described in Claims 2 through 4, it becomes possible to produce a fish scale liquid in which fish scales are dispersed or dissolved uniformly, and the obtained fish scale liquid has a dramatically reduced fish scale odor.

[0049] With the invention described in Claim 5, in addition to the aforesaid effects, the fish scale odor can be further reduced.

[0050] With the invention described in Claim 6 or 7, it becomes possible to provide processed food that effectively utilizes the nutritional constituents of fish scales and also that has a dramatically reduced fish scale odor.